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STANDARDIZATION OF STATIONARY SOURCE METHOD FOR VINYL CHLORIDE

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

A program was conducted to evaluate the proposed EPA Method 106 - Determination of Vinyl Chloride from Stationary Sources. Vinyl Chloride samples in Tedlar bags remain stable for more than one week. Aluminized Mylar bags can also be used if the samples are analyzed within two days. Several compounds can interfere with the gas chromatographic analysis by forming a single unresolved peak with vinyl chloride. Acetaldehyde and ethylene oxide are serious interferences with methanol and isobutane interfering under some conditions. Retention indices have been measured for several compounds on three useful GC columns. Nearly all samples can be satisfactorily resolved with the proper choice of column. Pressurized gas cylinders of vinyl chloride in nitrogen were used for calibrations. The cylinders were standardized against gravimetrically calibrated vinyl chloride permeation tubes. Field tests were also made at a polyvinyl chloride plant and a vinyl chloride monomer plant. No serious problems with the method were found in the field tests.

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STANDARDIZATION OF STATIONARY SOURCE METHOD FOR VINYL CHLORIDE

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FOREWORD

Midwest Research Institute, under Task 7 of EPA Contract No. 68-02-1098, conducted in-house work toward the standardization of Method 106 - Determination of Vinyl Chloride From Stationary Sources. Upon completion of the method evaluation, field tests at a polyvinyl chloride plant and a vinyl chloride monomer plant were conducted under Task 9 of the contract. Measurements of retention indices of interfering compounds were done under Task 5 of EPA Contract No. 68-02-1780. This report contains the results of the Method 106 laboratory evaluation and of the field tests of the method.

Approved for:

MIDWEST RESEARCH INSTITUTE

M. P. Schuck

for W. J. Shannon, Director
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Sciences Division

August 22, 1977

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ABSTRACT

Method 106 - Determination of Vinyl Chloride From Stationary Sources - was evaluated for possible problems with sample stability, interferences and methods of standardization. The method was then field tested at a polymer plant incinerator and a monomer plant scrubber. Vinyl chloride field samples were found to be stable in Tedlar bags for periods of greater than 1 week. Laboratory tests revealed that aluminized Mylar bags also worked well if the samples were analyzed within 24 to 48 hr. Several compounds can interfere with the gas chromatographic analysis. Acetaldehyde and ethylene oxide are the primary inteferences. Under some conditions methanol and isobutane also interfere. Retention indices measured on the three most promising columns indicate that most samples can be successfully resolved. Pressurized gas cylinders of vinyl chloride in nitrogen were found to have excellent long-term stability, and a gravimetrically calibrated vinyl chloride permeation tube is an excellent primary standard. The field tests indicated no serious problems with the procedure and demonstrated that vinyl chloride had excellent stability in the presence of HCl, Cl_2, H_2O, and other reactive compounds.

This report was submitted in fulfillment of Tasks 7 and 9 of Contract No. 68-02-1098 and in partial fulfillment of Task 5 of Contract No. 68-02-1780 by Midwest Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from January 1975 to December 1976, and work was completed as of January 1977.

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This work was conducted under the technical management of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of Midwest Research Institute's Environmental and Materials Sciences Division, who is the program manager. Dr. George Scheil was task leader. He was assisted by Mr. George Cobb of Midwest Research Institute. The assistance of Mr. William Roberts of the Shell Chemical Company during the field test is gratefully acknowledged.

SECTION I

INTRODUCTION

On December 24, 1975, under Section 112 of the Clean Air Act as amended, the Environmental Protection Agency (EPA) added vinyl chloride to the list of hazardous air pollutants[1/] because it has been implicated as the causal agent of angiosarcoma and other serious disorders. A national emission standard has been promulgated[2/] that covers plants that manufacture ethylene dichloride, vinyl chloride and polyvinyl chloride (PVC). These regulations include a method for determining vinyl chloride emissions from stationary sources, EPA Method 106. The Quality Assurance Branch of the Environmental Monitoring and Support Laboratory at Research Triangle Park, North Carolina, has as its task the evaluation and standardization of EPA source test methods. While participating in this program, Midwest Research Institute (MRI) has undertaken a study of EPA Method 106.

This report covers the laboratory evaluation and field testing conducted by MRI of Method 106 - Determination of Vinyl Chloride from Stationary Sources. The testing was done for EPA under Contract No. 68-02-1098, "Standardization of Stationary Source Emission Measurement Methods." This report includes Task 7, Laboratory Evaluation, and Task 9, Field Testing. Additional laboratory testing was done under Task 5 of EPA Contract No. 68-02-1780.

Method 106 is intended for use in both vinyl chloride monomer plants and PVC plants. When testing the exit of an incinerator-type control device, the level of organics is low and generally consists of only a few compounds. Other control devices or ventilator ducts can contain a very complex mixture of compounds with many constituents being at concentrations equal to or greater than the vinyl chloride concentration. Thus, the primary problem in analysis of vinyl chloride can often be the satisfactory resolution of vinyl chloride from other possible constituents.

1/ Federal Register, 40, 59477, December 24, 1975.
2/ Federal Register, 41, 46564-46573, October 21, 1976.

The following sections of this report examine the laboratory evaluation of Method 106, including sample stability, interferences, methods of standardization, and finally the results of field tests of the method at a polymer plant incinerator and a monomer plant scrubber.

SECTION II

LABORATORY METHOD EVALUATION

The originally proposed Federal Register procedure is given in Appendix A. Three possible problem areas were examined in some detail: a reliable standardization procedure, satisfactory separation of interferences, and the stability of vinyl chloride samples. These and other problems are discussed in detail in the following sections.

VINYL CHLORIDE STANDARDIZATION

Because of the strict safety regulations necessary for handling pure vinyl chloride, the primary calibration procedure cannot be used in many situations. The alternate procedure using gas cylinders containing 15 to 150 mg/m^3* (5 to 50 ppm) vinyl chloride mixtures in nitrogen can be used with less stringent precautions. However, the accuracy and stability of calibration gases can be poor if sufficient care is not taken during their preparation. A reliable method of verifying the cylinder concentrations is then necessary. The dilution of pure vinyl chloride in a calibrated dynamic dilution system is possible, as well as the injection of vinyl chloride into a Tedlar bag as given in the method. A vinyl chloride permeation tube assembly allows a reliable, reasonably safe calibration and was used as the primary calibration standard in all project work. With a standard water-heating bath supplying water at 30.0 $\pm$ 0.1°C to the water jacket of a straight-tube condenser, a simple permeation tube assembly was constructed. The permeation rate through the Teflon walls of the permeation tube is dependent almost solely on temperature. Carrier gas flow rate or most other variables have no effect on permeation rate as long as liquid vinyl chloride remains in the tube. By periodically weighing the tubes on an analytical balance the rate of release can be calculated. Table 1 summarizes the calibration data for three sets of two 100 mm (1.0 mm wall) permeation tubes. While the apparent weight loss over a few days can vary widely, due

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* Specified at conditions of 293°K and 101.3 kPa (760 mm Hg). To convert from parts per million (v/v) to milligrams per cubic meter at this temperature and pressure, multiply by 2.59.

TABLE 1. PERMEATION TUBE CALIBRATIONS

Date	Time	Weight loss (mg) Tube No. 1	Weight loss (mg) Tube No. 2	µg/min of Vinyl chloride Tube No. 1 Since previous weighing	Tube No. 1 Cumulative	Tube No. 2 Since previous weighing	Tube No. 2 Cumulative
3-28-75	1645	--	--	--	--	--	--
4-1-75	1600	12.52	16.64	2.19	2.19	2.91	2.91
4-4-75	1625	15.28	13.15	3.52	2.76	3.03	2.96
4-8-75	1645	13.57	15.87	2.35	2.61	2.75	2.88
4-9-75	1635	4.16	2.22	2.94	2.66	1.55	2.75
4-11-75	1635	6.87	8.51	2.38	2.58	2.96	2.89
4-15-75	1615	16.52	15.70	2.88	2.65	2.74	2.86
4-18-75	1615	11.06	12.08	2.55	2.63	2.80	2.85
4-21-75	1505	12.23	14.45	2.88	2.67	3.40	2.92
4-25-75	1030	14.27	13.28	2.60	2.66	2.42	2.85
4-30-75	1635	24.76	22.56	3.27	2.76	2.98	2.87
5-2-75	1615	4.85	8.08	1.70	2.70	2.83	2.87
5-6-75	1635	16.05	16.68	2.77	2.70	2.89	2.87
5-9-75	1640	11.19	12.00	2.59	2.70	2.77	2.86
5-13-75	1500	16.18	16.26	2.86	2.71	2.87	2.86
5-16-75	1530	15.12	13.92	3.46	2.76	3.20	2.88
5-27-75	1510	40.49	46.19	2.56	2.72	2.92	2.89
6-3-75	1635	28.93	27.45	2.85	2.73	2.70	2.87
6-6-75	0825	10.62	10.88	2.77	2.74	2.84	2.87
6-10-75	1440	17.10	17.87	2.79	2.74	2.91	2.87
6-13-75	1515	12.18	12.71	2.79	2.74	2.92	2.87
6-25-75	0950	47.31	48.83	2.79	2.75	2.88	2.87
7-2-75	1020	28.19	29.46	2.79	2.75	2.91	2.88
7-11-75	0900	36.46	36.95	2.83	2.76	2.87	2.88
7-18-75	0830	27.03	29.30	2.69	2.75	2.92	2.88
7-29-75	1000	44.58	45.91	2.80	2.76	2.88	2.88
9-9-75	1100	170.44	175.49	2.82	2.77	2.90	2.88
9-18-75	1150	34.32	36.76	2.65	2.77	2.84	2.88

(continued)

TABLE 1 (continued)

Date	Time	Weight loss (mg) Tube No. 1	Weight loss (mg) Tube No. 2	µg/min of Vinyl chloride Tube No. 1 Since previous weighing	Tube No. 1 Cumulative	Tube No. 2 Since previous weighing	Tube No. 2 Cumulative
New Set of Tubes							
10-9-75	1640	--	--	--	--	--	--
1030-75	0835	81.53	83.55	2.74	2.74	2.81	2.81
11-10-75	1510	46.06	47.17	2.84	2.77	2.91	2.84
11-25-75	1630	59.46	61.46	2.74	2.76	2.83	2.84
12-18-75	1425	88.81	91.37	2.69	2.74	2.77	2.82
New Set of Tubes							
6-18-76	1025	--	--	--	--	--	--
6-28-76	1010	36.45	35.99	2.53	2.53	2.50	2.50
10-8-76	1450	379.62	370.28	2.58	2.58	2.52	2.51

to dust on the tubes or the test tubes used to hold them during weighing, the cumulative permeation rate remains constant for several months within 1 to 2%.

The calibration assembly is shown in Figure 1. The optional dilution gas was normally kept plugged off and was used only for low levels of vinyl chloride when the main rotameter could not supply enough nitrogen. A Singer charcoal test meter was then used to measure the additional dilution nitrogen.

The permeation tubes were supplied by two companies: Metronics Associates, Inc., Palo Alto, California, and AID, Inc., Avondale, Pennsylvania. The AID tubes are slightly larger in diameter with a longer life span but 7 of 12 of the tubes (one batch of four were good; a second set of eight had one good tube) had contamination present and polymerized within a few days. No problems were experienced with the set of four tubes from Metronics. A 3.2 mm (1/8 in.) O.D. Teflon tube was used to withdraw gas from the permeation assembly and the gas was pulled through the gas chromatograph sampling valve with a small vacuum pump at 20 to 50 ml/min.

Three gas cylinders supplied by Scott Environmental Technology, Inc., Plumsteadville, Pennsylvania, were checked against the permeation tubes. On three separate days the 12.9 mg/m^3 cylinder gave 12.3, 12.4, and 12.5 mg/m^3 vinyl chloride. The average, 12.4 mg/m^3, was assigned as the true value. The 25.6 and 117 mg/m^3 cylinders were checked once and showed 23.5 and 108 mg/m^3, respectively. All results are the averages of at least three measurements. No nonlinearity was found in response from 1 to 120 mg/m^3. All readings were by peak height, which was used in the original Method 106 procedure.

A permeation tube comparison is an excellent primary calibration for gas cylinders. Although the permeation assembly is not portable, and some tubes polymerize, the gravimetric calibration of the tubes is an absolute reference and the permeation rate is constant over the life of the tube. The calibration is necessary only for new cylinders with a check every 6 months or so after the initial calibration.

INTERFERENCES

Table 2 lists several compounds which might be present in vinyl chloride process streams together with their retention indices on a Chromosorb 102 column, 2 m x 3.2 mm (1/8 in.) O.D.* stainless steel at 100°C and on two modified columns. The only serious interferences are acetaldehyde and ethylene oxide which are usually not resolvable from vinyl chloride on a

* All chromatographic columns had a wall thickness of ~ 0.5 mm (0.020 in.).

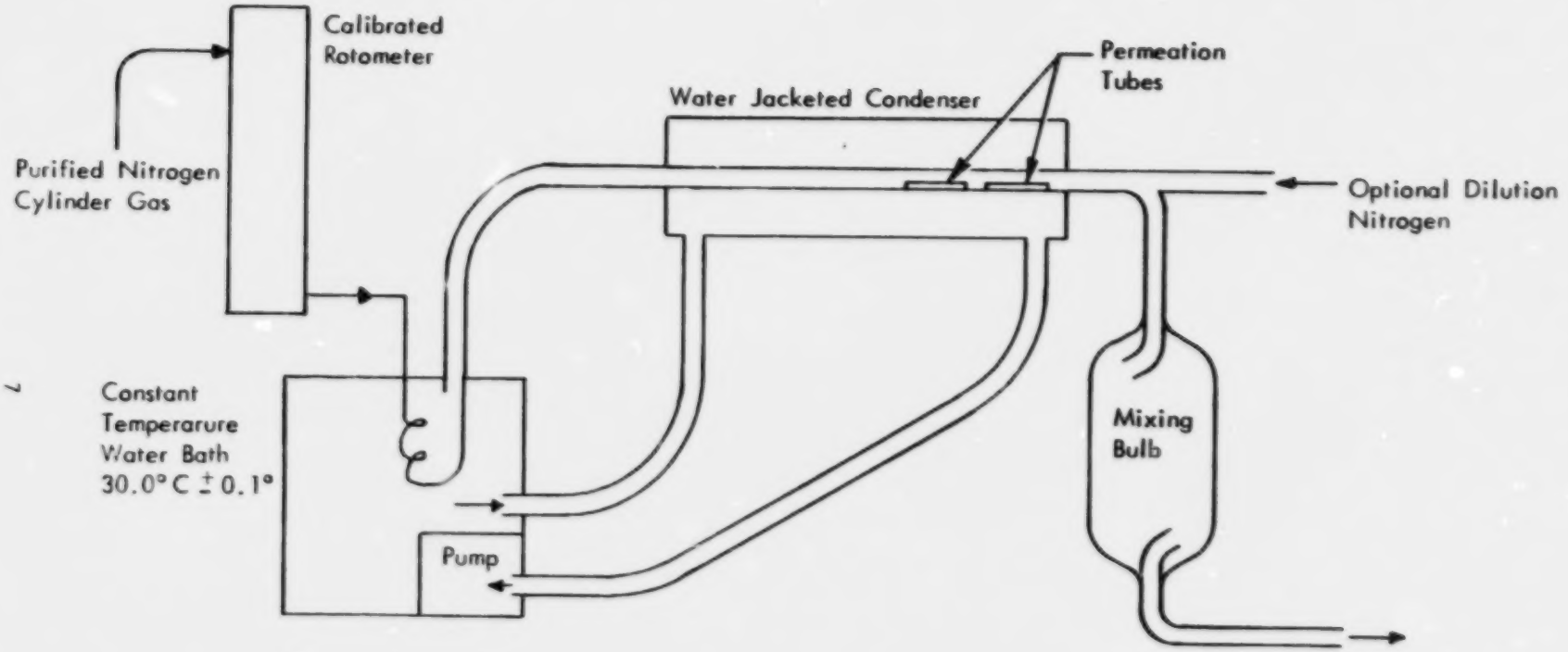

Figure 1. Vinyl chloride permeation assembly

TABLE 2. RETENTION INDICES FOR POSSIBLE VINYL CHLORIDE INTERFERENCES

	2 m Chromosorb 102 100°C	2 m Chromosorb 102 + 1 m Porapak T 120°C	2 m Chromosorb 102 + 2 m SF-96 120°C	2 m Chromosorb 102 + new 2 m SF-96 120°C
Methane*	100	100	100	100
Ethylene	180	180	175	-
Ethane*	200	200	200	200
Propane*	300	300	300	300
Methyl chloride	320	340	320	325
Methanol	330	395	350	375
Acetaldehyde	355	400	375	(low levels retained) 400
Ethylene oxide	355	395	375	(low levels retained) -
Vinyl chloride	360	375	360	(low levels retained) 360
Isobutane	380	380	380	380
Isobutylene	395	395	385	390
1-Butene	395	395	395	-
n-Butane*	400	400	400	400
1,3-Butadiene	400	410	395	395
trans-2-Butene	400	410	400	-
Ethanol	415	475	435	-
Ethyl chloride	415	430	415	410
cis-2-Butene	415	415	410	-
1,1-Dichloroethylene	480†	490†	480†	-
trans-1,2-Dichloroethylene	510†	495†	505†	-

* Reference compounds for indices.
† Column at 150°C.

2 m column. Acetaldehyde can be present in significant amounts[3] in process streams. (Ethylene oxide appears to be converted to acetaldehyde on the GC columns.) The use of a precolumn containing sodium bisulfite has been suggested to remove acetaldehyde.[3] However, in MRI's tests the removal was not always complete and the precolumn can be inactivated by many other compounds so that the removal efficiency can change suddenly during a series of analyses.

No single column is likely to resolve all possible interferences. However, since no known interference with a retention time identical to vinyl chloride at 100°C on Chromosorb 102 has been found, the presence of unresolved interference peaks can be detected by a comparison of the quantitative results by peak height and by peak area. If the results by both methods are the same, then the peak is probably pure vinyl chloride. If peak height has a lower result than peak area, an interference is present and a second column should be added after the Chromosorb 102. The second column takes advantage of the separation already obtained on the Chromosorb 102 column by separating the particular interfering compound(s) without obtaining a significant shift of the other peaks in the chromatogram. A 2 m x 3.2 mm (1/8 in.) O.D. stainless steel column packed with 20% SF-96 on acid-washed 60/80 mesh Chromosorb P has been found to retard acetaldehyde, which elutes as a broad peak immediately following vinyl chloride. This combination column was used during most of MRI's field tests of the method. However, resolution of methanol and vinyl chloride is not good. Since methanol tends to elute as a severely tailing peak it will usually cause only a change in baseline. Three percent columns of other similar[4] columns (OV-1, OV-101) do not provide enough separation at the 100°C operating temperature of Chromosorb 102.

Present evidence indicates that the separation depends partially upon the high loading of liquid phase on the column and upon unique differences between SF-96 and other nonpolar liquid phases. Although Chromosorb P is not a high performance support, it does allow heavier loadings than newer supports, such as Chromosorb W or Chromosorb 750. The high loading allows reasonable separation at 100°C, saturates the active sites of the support, and improves the reproducibility of results from one column to another.

The last column in Table 2 shows selected retention indices measured using a newly prepared and conditioned SF-96 column. The only compounds which show significant changes are acetaldehyde, ethylene oxide, and the alcohols. All of these compounds are strongly adsorbed by the column and elute as observable peaks only at concentrations above about 0.1%. At lower levels they will probably not be eluted as peaks but only as gradual baseline changes, unless the column has become partially deactivated by long

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3/ Krishen, A., and R. Tucker, Anal. Chem., 48, 455-456 (1976).

4/ Supina, W., The Packed Column in Gas Chromatography, Supelco, Inc. (1974).

use, as in the case of the older SF-96 column results. If large amounts of these compounds, especially methanol, are present, the use of a different column would be preferable. However, a 1 m section of Porapak S followed by 1 m of Porapak T has been shown to achieve good separation[5/] although isobutane may be shifted enough to interfere.

Further tests by MRI have revealed that Porapak S will not separate vinyl chloride and acetaldehyde (see Figure 2). A 1 m x 3.2 mm (1/8 in.) O.D. stainless steel column packed with 80/100 mesh Porapak T added after the Chromosorb 102 column does obtain a clean separation of vinyl chloride and acetaldehyde (Figure 3). However, isobutane is now very difficult to resolve from vinyl chloride. Operating the combined columns at 120°C should maintain good resolution with an analysis time comparable to the Chromosorb 102 column alone at 100°C.

The suggested analysis procedure is to compare results by height and area on the Chromosorb 102 column. If the height result is lower, then a second column (SF-96 or Porapak T) is added after the Chromosorb 102 column and chromatographic conditions adjusted until the interfering peak is resolved, height and area results agree, and all other nearby peaks on the initial column can be definitely accounted for in the modified chromatogram. Table 2 should be used to choose the proper secondary column.

The best method of confirming purity of a suspect peak is mass spectrometry, a procedure which is not suitable for routine analysis. An alternate possibility is an electron capture detector which has a strong response to vinyl chloride, very little response to acetaldehyde and hydrocarbons. This method is very carrier-flow rate sensitive and can be used only under stable laboratory conditions.

SAMPLE STABILITY

As indicated in Section III of this report, vinyl chloride samples in Tedlar bags have been found to decay at a rate of less than 10%/month even in complex samples. Teflon bags have no economic advantage over Tedlar and are not good vapor barriers, thus Teflon sample bags are not suitable for vinyl chloride samples. Aluminized Mylar has been suggested as an alternative.[6/] In a test of Tedlar and aluminized Mylar bags at the level of 15 mg/m^3 vinyl chloride, both materials showed less than 5% loss of vinyl chloride over a 2-week period. However, at the end of that period, outgassing from the Mylar resulted in several peaks of very long retention time

5/ Mr. William Roberts, Shell Chemical Company, Houston, Texas, Private Communication.

6/ Levine, S. P., K. G. Hebel, J. Bolton, Jr., and R. E. Kugel, Anal. Chem., 47, 1075A-1080A (1975).

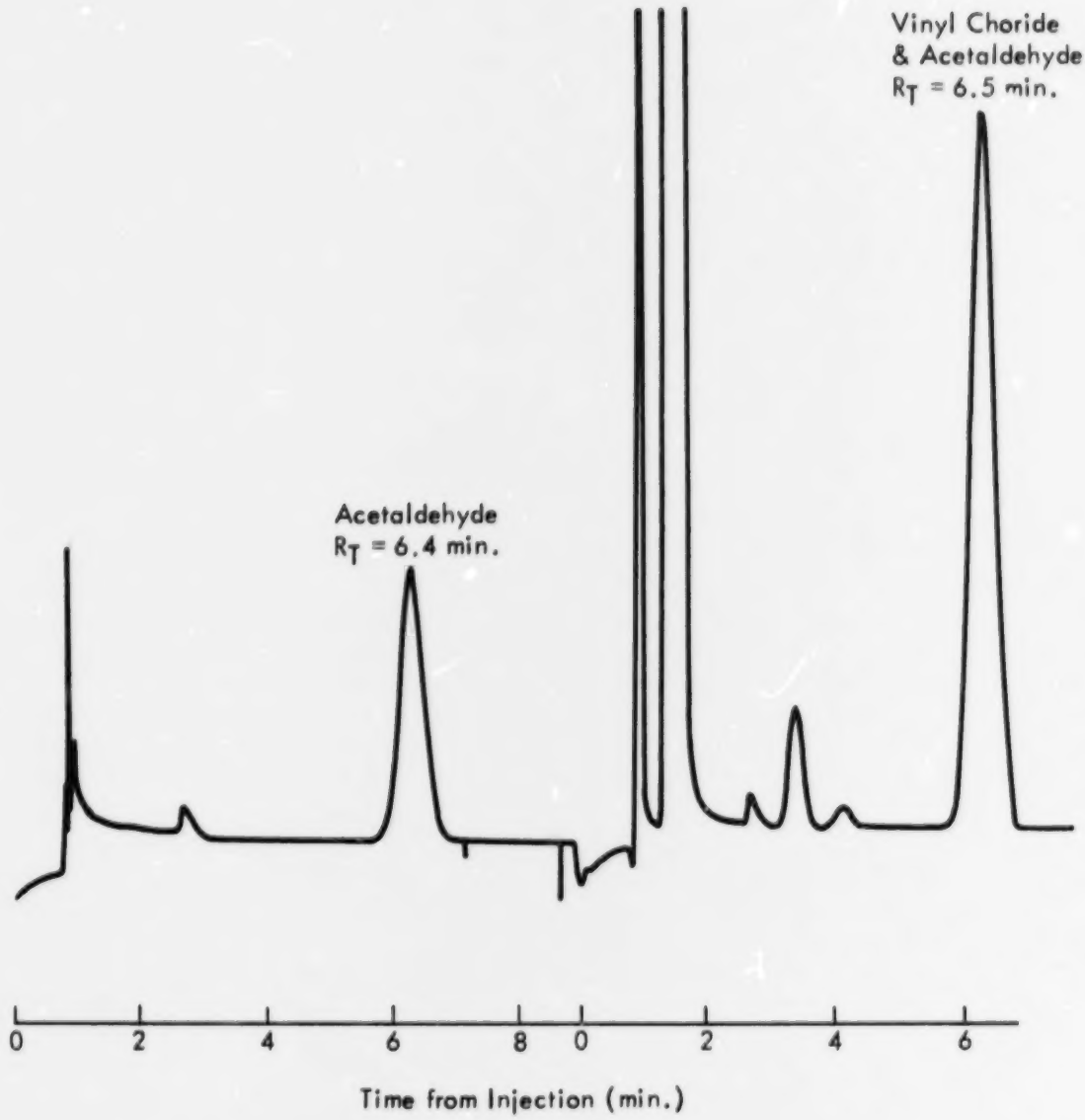

Figure 2. Retention time determination on 2 m Chromosorb 102 plus 1 m Porapak S at 110°C

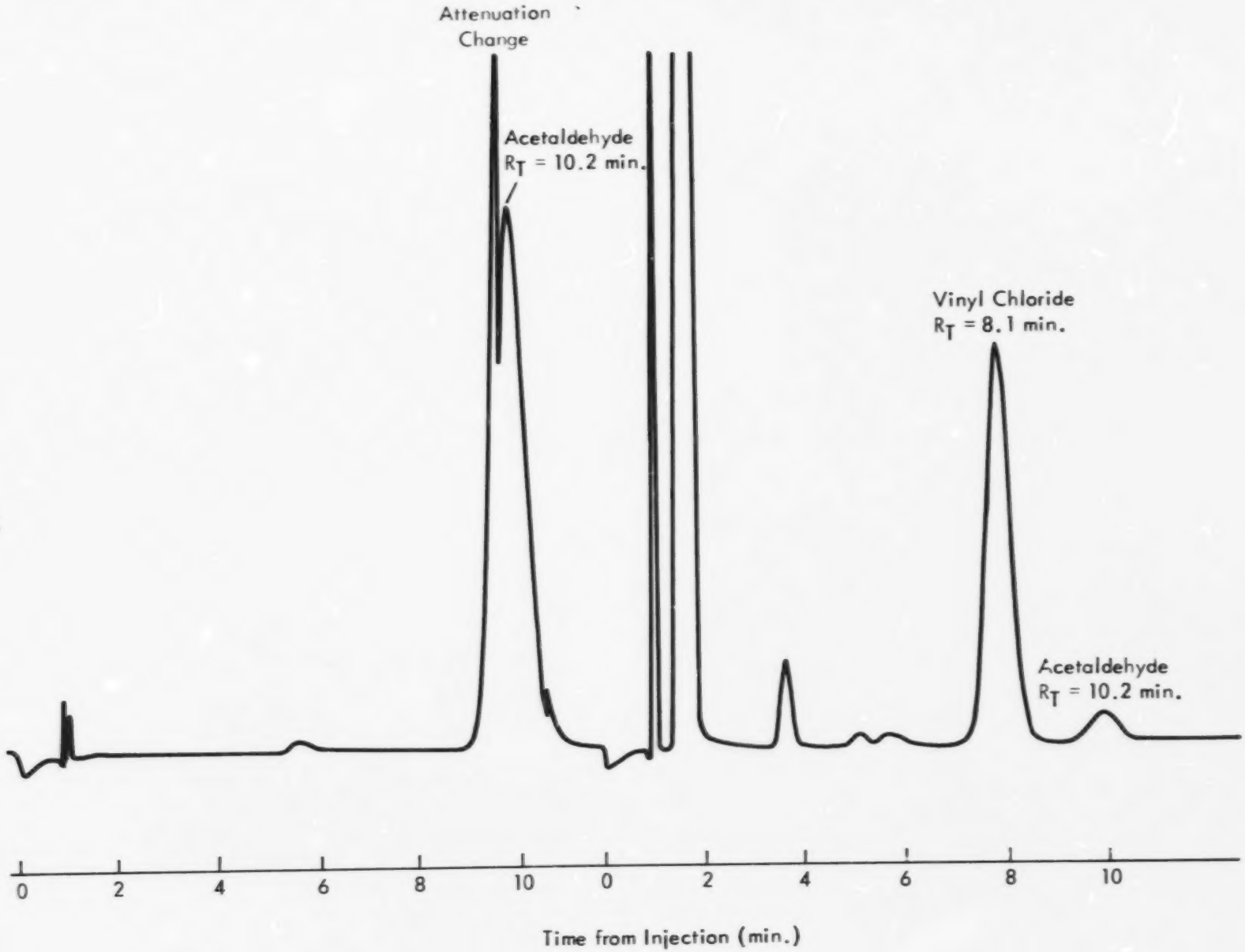

Figure 3. Retention time determination on 2 m Chromosorb 102 plus 1 m Porapak T at 110°C

(~ 1 hr at 100°C). Unless the chromatograph can be backflushed or programmed after elution of vinyl chloride, aluminized Mylar bag samples should always be analyzed quickly. Mylar bags are about half as expensive as Tedlar but are commercially available from only one known source, Calibrated Instruments, Inc., Ardsley, New York. The Mylar, aluminum foil, vinyl outer film laminate used is, however, an excellent vapor barrier and is more flexible and durable than Tedlar.

While Tedlar should remain as the primary bag material, the use of aluminized Mylar is also acceptable if the analyst is aware of the limitations of aluminized Mylar.

OTHER CONSIDERATIONS

Several other changes have been made in the version of Method 106 which was developed by MRI based on the results of this study. This version is given in Appendix B. The column temperature, 155°C, of the proposed method is too high, from the standpoint of unnecessary column bleed and low resolution due to a short retention time. Temperatures of 100 to 110°C have been used in MRI's work and provide a reasonable retention time of about 4 to 5 min at 25 ml/min with very low bleed (and noise). The Varian 2440 chromatograph used has a detection limit of ~ 100 $\mu g/m^3$ (x2 noise) when operating at 100°C with a 2 ml sample loop volume.

Additional leak checks have also been added to improve the reliability of the sampling bags and enclosures. An optional glass condensate trap has been added for the significant fraction of sources with condensibles present. The simple vacuum traps have proved reasonably rugged and very efficient in reducing the sample dew point without causing undue absorption of vinyl chloride.

A more significant change is the placement of the rotameter (made of glass or stainless steel for sample compatibility) between the sample bag and the probe. If the rotameter is made of glass and stainless steel, sample contamination or reaction is improbable and the condenser protects the rotameter from condensation. But the change in position of the rotameter significantly increases the probability of obtaining a representative sample. Even with the added leak checks, many bags have failed to fill or filled with ambient air during MRI's tests with this and derivative methods when the rotameter is after the pump. The pump pulsations cause inaccurate readings, but more serious is the fact that a slight leak in the bag, enclosure, pump or connecting tubing and fittings can cause a properly run test to fail because a very small leak will allow in enough ambient air to greatly reduce the sample flow rate into the sample bag. With the rotameter before the sample bag only a leak in the sections ahead of the rotameter will foul a test. A leak anywhere else will be more obvious, and may not even stop the test if it is reasonably small and constant and is in the enclosure or pump, since then the bag will still fill with a slightly higher

pumping rate. Most important, the rotameter can now show that gas is going into the bag (although the bag can still leak) and not merely that gas is passing out of the pump. The relocation of the rotameter reduces by at least 50% the number of fatal leak points, a very important factor in a system which must operate at subambient pressures.

SECTION III

FIELD TESTING

Two sources were chosen to field test the method. One test was at a vinyl chloride polymer plant which used an incinerator/scrubber to destroy vinyl chloride. The second test was at Shell Chemical Company, Deer Park, Texas. The stack from their vinyl chloride monomer plant oxychlorination vent was sampled. This stream was very complex, containing significant amounts of ethylene, chlorine, hydrogen chloride, acetaldehyde, methyl chloride, ethyl chloride, dichloroethane, etc. The presence of large amounts of high-boiling compounds required the use of a backflush valve. All equipment for these tests was loaded into a van and driven to the sites where the gas chromatograph was then set up inside the van. Both tests were made in a single trip. Due to the safety problems and difficult access, stack flow rate measurements were not made for either test. To remove some of the acid gases possibly present in both streams, a section of tubing packed with granular potassium carbonate was used to remove Cl_2 and HCl. A laboratory test showed that the potassium carbonate had no effect on vinyl chloride levels.

TEST AT A VINYL CHLORIDE POLYMER PLANT INCINERATOR

The unit tested was an incinerator-scrubber unit which handled process off-gases from a PVC operation. The gases are stored in holding tanks and then pumped to the incinerator whenever the tanks are full. The incinerator is then started and continues to operate until the holding tanks are empty. The operating time can vary from 1/2 hr to several hours depending on the level of activity in the polymer operation. The gas-fired incinerator is followed by an alkali scrubber which vents through a stack. The stack is mounted on top of the scrubber and has an exit height of about 15 m. Two 150 mm (6 in.) flanges are mounted to the stack at a height of 10.5 m above ground level.

A bored-through 1/4 in. NPT to 1/4 in. Swagelok male connector was mounted in one of the flanges and a section of 6.4 mm (1/4 in.) O.D., Teflon-lined stainless steel tubing was slipped through the connector so that the end of the tubing was at the center of the 300 mm diameter stack.

The probe tip was packed with glass wool before being inserted. The sample line was then connected to the probe tubing with an elbow fitting. The sample line consisted of a 15 m section of 6.4 mm (1/4 in.) O.D. Teflon-lined stainless steel tubing inside a sheath of 12.7 mm (1/2 in) O.D. copper tubing. A steam line was connected to the outer tube by a 12.7 mm (1/2 in.) tee at ground level and the probe end of the sheath was left open so that a continuous flow of steam passed through the sheath to prevent condensation in the sample line. The sample probe and line had to be installed with a "cherry picker" crane, since no ladder or other access was available on the small diameter stack. The bottom end of the sample line was connected to the center tube of a 20 mm x 200 mm glass vacuum trap which was immersed in an ice bath. A 150 mm section of 6.4 mm (1/4 in.) O.D. stainless steel tubing packed with granular potassium carbonate followed the condenser, and the sample stream was then split three ways. Two integrated bag samples were obtained in parallel, and on the 2nd day direct GC sampling was made on the sample stream. The remaining parts of the trains were as given in the procedure given in Appendix B.

The equipment was set up on June 3, 1976, and a pair of samples was obtained that day and analyzed on the following day. The Chromosorb 102 column was used for all tests and operated at 110°C.

One bag on June 4 was found to be contaminated, but the other three for that day, one set of bag samples the 1st day, and the direct GC sampling were consistent with a vinyl chloride concentration of 0.25 ± 0.1 mg/m^3. Table 3 shows the results of the tests. Figure 4 is a sample chromatogram. Due to the very small quantities of vinyl chloride present, peak height was used instead of area. Approximately 5 ml of water condensate was obtained from a total gas volume of 200 liters. After returning to MRI the condensate was analyzed by GC and no organic matter was detected in the water. One integrated gas bag sample was returned to MRI for stability measurements.

The sample contains no acetaldehyde or other known interferences. The condensate sample was found to contain 0.0037 M chloride.

TEST AT A VINYL CHLORIDE MONOMER PLANT

On June 8 through 10, further field testing was done on a vinyl chloride monomer oxychlorination vent at the Shell Chemical Company in Deer Park, Texas. The sampling platform on this stack is approximately 15 m above the ground. The sample line was connected to the stack through a 2.54 cm (1.0 in.) gate valve. A tee connection at the platform allowed sampling at the platform as well as at ground level via the heated sample line. The sample line was connected to the stack in a manner similar to that used on the first test except that the truck containing the gas chromatograph could not be parked close enough to the stack to allow direct GC sampling. One pair of samples was taken at ground level. Three pairs of samples were obtained with one sample taken at ground level and one at the sampling platform. The analysis

TABLE 3. TEST RESULTS - VINYL CHLORIDE INCINERATOR

Sample	Time	Attenuation	Peak heights	Vinyl chloride concentration (mg/m^3)
6-3-76 analyzed on 6-4-76				
23.5 mg/m^3 standard		4×10^{-12}	76.5, 74.7, 75.3	
Bag No. 1	1410-1500	1×10^{-12}	4.0, 2.7	0.28
Bag No. 3	1410-1500	1×10^{-12}	3.2, 3.8	0.28
6-4-76				
Direct sampling	0955	2×10^{-12}	1.0	0.16
Direct sampling	1000	2×10^{-12}	1.0	0.16
Direct sampling	1007	2×10^{-12}	1.0	0.16
Direct sampling	1014	2×10^{-12}	1.0	0.16
Direct sampling	1020	2×10^{-12}	1.0	0.16
Direct sampling	1027	2×10^{-12}	1.0	0.16
Direct sampling	1034	2×10^{-12}	1.0	0.16
Direct sampling	1041	2×10^{-12}	0.8	0.13
Direct sampling	1048	2×10^{-12}	0.8	0.13
Bag No. 4	0954-1054	1×10^{-12}	5.0, 4.5	0.41*
Bag No. 2	0954-1054	1×10^{-12}	2.5, 2.0	0.18
23.5 mg/m^3 standard		4×10^{-12}	66.4, 67.6, 66.8	
Bag No. 1	1225-1310	1×10^{-12}	3.5, 3.2, 3.2	0.28
Bag No. 3	1225-1310	1×10^{-12}	2.5, 2.5, 2.5	0.21
Reanalysis of Bag No. 2 from 6-4-76 on 6-24-76		1×10^{-12}	2.5, 3.0	0.17
12.4 mg/m^3 standard		4×10^{-12}	46.8, 46.6	
Reanalysis of Bag No. 2 from 6-4-76 on 7-27-76		1×10^{-12}	5.0, 4.5	0.28
12.4 mg/m^3 standard		4×10^{-12}	47.5, 47.0	

* Artifact peaks present.

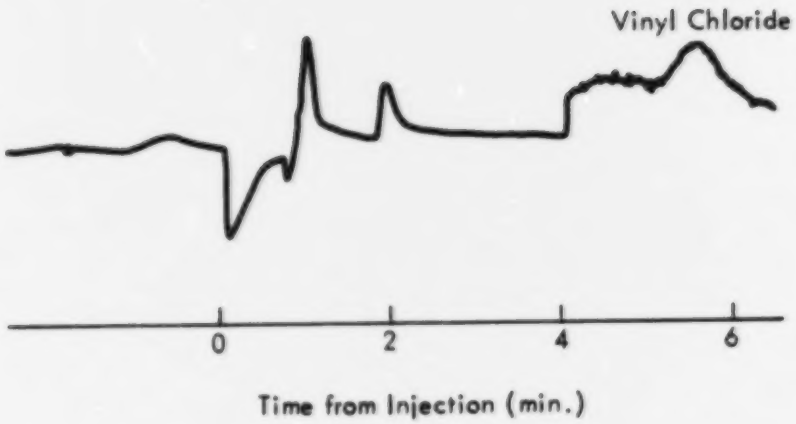

Figure 4. Sample Chromatogram Bag No. 3, June 4, 1976, vinyl chloride = 80 ppb

results are given in Table 4. Sample chromatograms are shown in Figure 5, which compares the different columns and the effect of a sodium bisulfite scrubber.

Condensate samples were analyzed for vinyl chloride after returning to MRI. The levels varied from ~ 3 μg/g to less than 0.5 μg/g. Approximately six times as much acetaldehyde was present and varying amounts of other organic compounds were also present, primarily alcohols, judging by the odor given off by the samples. A sample chromatogram is shown in Figure 6. Chloride analyses were made on these condensate samples and the results are shown in Table 4. The volume of condensate was always less than 1 ml. The sampling was done from an existing tap about 15 m above ground. The connection was to a gate valve on a 1 in. NPT pipe which allowed the sample probe to be inserted to the stack center. Stack diameter was about 3 m at the sample point, midway through a tapered section of the stack.

Sample backflush to vent was used to remove several slow eluting compounds from the samples. The backflush valve was thrown after elution of the vinyl chloride peak and was flushed for a slightly longer time than the time from sample injection to when backflushing began. A Carle double sampling loop valve was maintained at 97°C for all analyses. Matched sample loops were used with volumes of 2 ml.

An attempt was made to split the column effluent for parallel FID and electron capture detection. However, the electron capture standing current could not be stabilized due to the backflushing and no usable data were obtained by electron capture.

Figure 7 is a sample chromatogram obtained by Shell Chemical on a logarithmic response recorder, programming from 60 to 190°C. The known components of the sample are identified. The column used was a 3.2 mm (1/8 in.) O.D. x 3 m Chromosorb 102. Shell used these conditions for all of their analyses. They used a midget impinger containing a 5% solution of sodium bisulfite to remove acetaldehyde. They also obtained their samples in small evacuated propane cylinders with a needle orifice to fill the cylinder at a constant rate.

The results of the laboratory and field tests have been incorporated into the suggested procedure given in Appendix B. The proof of a satisfactory separation of vinyl chloride and acetaldehyde removes the last major problem in the analysis. One of the columns suggested should be able to resolve most of the mixtures which occur in vinyl chloride monomer and polymer plants.

Method 106 was published in the Federal Register, Vol. 41, Thursday, October 21, 1976, pp. 46569-46571, before the final version of this report was completed. A copy of the procedure is given in Appendix C.

TABLE 4. VINYL CHLORIDE ANALYSIS RESULTS OF SAMPLING AT SHELL CHEMICAL COMPANY*
(all results reported as vinyl chloride, mg/m^3)

Date/time	Sample	Attenuation factor	Peak areas	MRI vinyl chloride result by area	Peak height	MRI result by height
6-8-76	108 mg/m^3 standard	16×10^{-12}	820, 813	-	66.9, 67.2	-
1030-1130	Bag No. 3 on ground	32×10^{-12}	1,050, 1,047	285	60.4, 59.8	197
1030-1130	Bag No. 4 on platform†	32×10^{-12}	667, 647	176	37.6, 36.8	122
6-9-76	108 mg/m^3 standard	16×10^{-12}	-	-	84.5, 84.5, 84.5	-
1000-1100	Bag No. 1 on platform	64×10^{-12}	514	264	38.9, 38.0, 37.5	205
1000-1100	Bag No. 3 on ground	64×10^{-12}	652, 647	334	47.1, 46.8	256
	108 mg/m^3 standard	16×10^{-12}	867, 845	-	76.9, 76.4	-
6-10-76	108 mg/m^3 standard	8×10^{-11}	1,884, 1,849	-	47.0, 47.2	-
0930-1030	Bag No. 3 on platform	8×10^{-11}	No organics found‡		-	-
0930-1030	Bag No. 1 on ground	8×10^{-11}	No organics found‡		-	-
1325-1425	Bag No. 3 on ground†	16×10^{-11}	2,165, 2,245, 2,155	254	55.0, 55.9, 53.0	262
1325-1425	Bag No. 1 on ground†	16×10^{-11}	2,190, 2,175	256	53.0, 52.5	254
	108 mg/m^3 standard	8×10^{-11}	1,895, 1,845	-	45.0, 44.8	-
Reanalysis of 6-24-76	Bag No. 1	8×10^{-11}	3,315	243	-	-
	Bag No.	8×10^{-11}	3,280, 3,340	243	-	-
	108 mg/m^3 standard	4×10^{-11}	2,950, 2,970, 2,995	-	-	-
	Bag No. 4	8×10^{-11}	1,325, 1,310	98	-	-
	108 mg/m^3 standard	4×10^{-11}	3,015, 3,030	-	-	-
Reanalysis of 7-27-76	Bag No. 3	8×10^{-11}	3,115, 3,165	225	-	-
	Bag No. 4	4×10^{-11}	2,470, 2,550	91	-	-
	Bag No. 1	8×10^{-11}	2,750, 2,790	199	-	-
	108 mg/m^3 standard	4×10^{-11}	3,065, 3,085	-	-	-

(continued)

TABLE 4 (continued)

Date/time	Sample	Analyses with sodium bisulfite trap for acetaldehyde removal: Peak areas	MRI result by area	Peak height	MRI result by height	Plant process analyzer	Shell lab result**	Condensate chloride concentration
6-8-76	108 mg/m^3 standard		-	-	-	-	-	-
1030-1130	Bag No. 3 on ground	976	262	50.4	166	259	264 (189)	-
1030-1130	Bag No. 4 on platform†	541, 536	145	30.8, 30.6	101	259	-	0.005 M
6-9-76	108 mg/m^3 standard	-	-	-	-	-	-	-
1000-1100	Bag No. 1 on platform	469, 500	251	34.5, 36.3	194	251	355 (262)	0.0014 M
1000-1100	Bag No. 3 on ground	629, 643	326	45.5, 46.2	251	251	275 (251)	-
	108 mg/m^3 standard	-	-	-	-	-	-	-
6-10-76	108 mg/m^3 standard	-	-	-	-	-	-	-
0930-1030	Bag No. 3 on platform	-	-	-	-	-	0††	0.0011 M
0930-1030	Bag No. 1 on ground	-	-	-	-	-	0††	0.0046 M
1325-1425	Bag No. 3 on ground†	-	-	-	-	316	329 (280)	0.0017 M
1325-1425	Bag No. 1 on ground†	-	-	-	-	316	-	-
	108 mg/m^3 standard	-	-	-	-	-	-	-
Reanalysis of 6-24-76	Bag No. 1	-	-	-	-	-	-	-
	Bag No. 3	-	-	-	-	-	-	-
	108 mg/m^3 standard	-	-	-	-	-	-	-
	Bag No. 4	-	-	-	-	-	-	-
	108 mg/m^3 standard	-	-	-	-	-	-	-
Reanalysis of 7-27-76	Bag No. 3	-	-	-	-	-	-	-
	Bag No. 4	-	-	-	-	-	-	-
	Bag No. 1	-	-	-	-	-	-	-
	108 mg/m^3 standard	-	-	-	-	-	-	-

* A 2 m x 3.2 mm (1/8 in.) O.D. Chromosorb 102 column was used on 6-8-76, and a 150-mm section of 6.4 mm (1/4 in.) O.D. stainless steel tubing packed with sodium bisulfite was used for acetaldehyde removal.
A 25 cm x 3.2 mm (1/8 in.) O.D. OV-101 column was added after the 2 m Chromosorb 102 on 6-9-76. Acetaldehyde still interfered and was removed with sodium bisulfite.
A 2 m x 3.2 mm (1/8 in.) O.D. Chromosorb 102 column followed by a 2 m x 3.2 mm (1/8 in.) O.D. SF-96 column was used at 110°C on 6-10-76 and all reanalyses. Acetaldehyde eluted approximately 1 min after vinyl chloride on this column as a broad tailing peak.
A test for oxygen content showed that a small leak was present somewhere in the line between the stack sample bag and (probably) the K_2CO_3 filter. The difference in oxygen showed about 20% air infiltration on the platform samples.

† Sample saved for reanalysis.

†† Leak in the sample line. Oxygen content 21%.

** Values in parentheses indicate results after acetaldehyde was removed by treatment with sodium bisulfite.

†† Shell lab analysis of MRI bag sample.

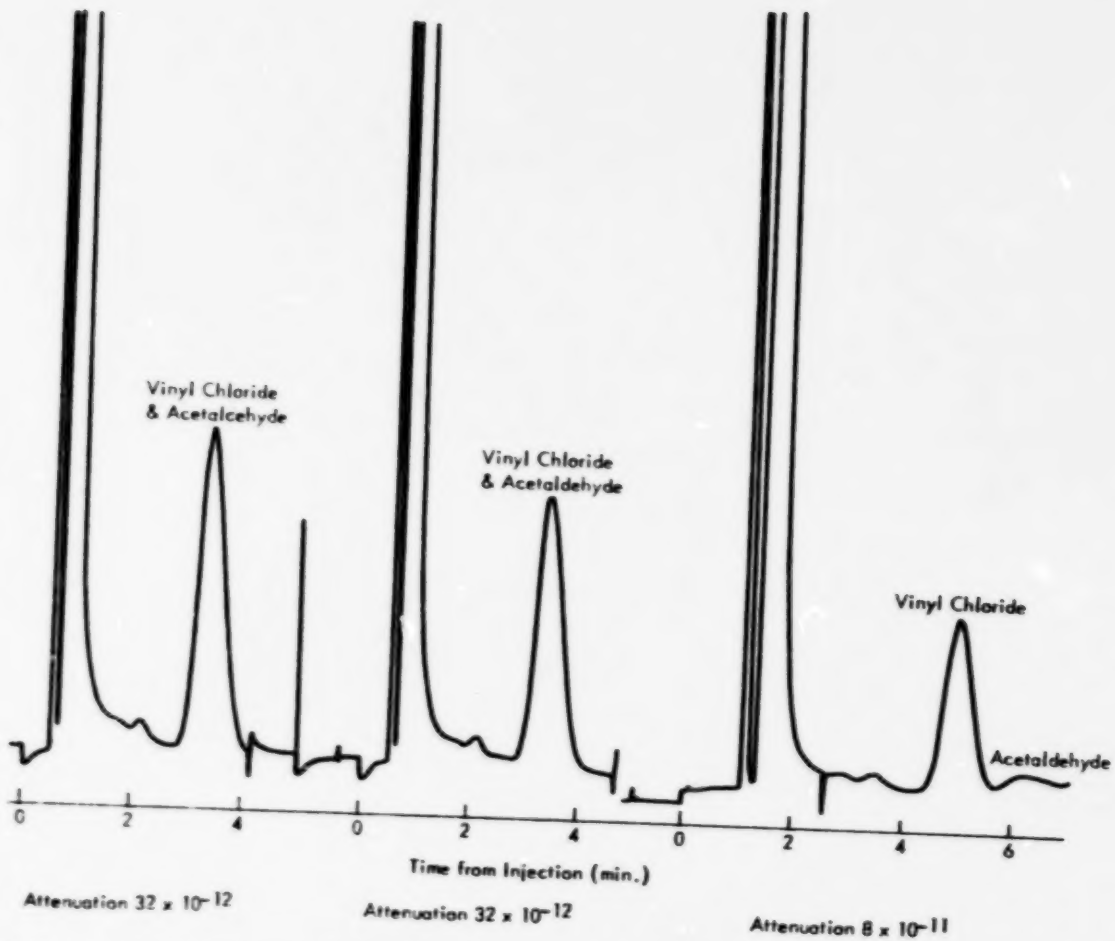

Figure 5. Bag No. 4 sample of June 8, 1976. First run on Chromosorb 102 column; second run, same column with sodium bisulfite. Last run on Chromosorb 102/SF-96 column June 24, 1976

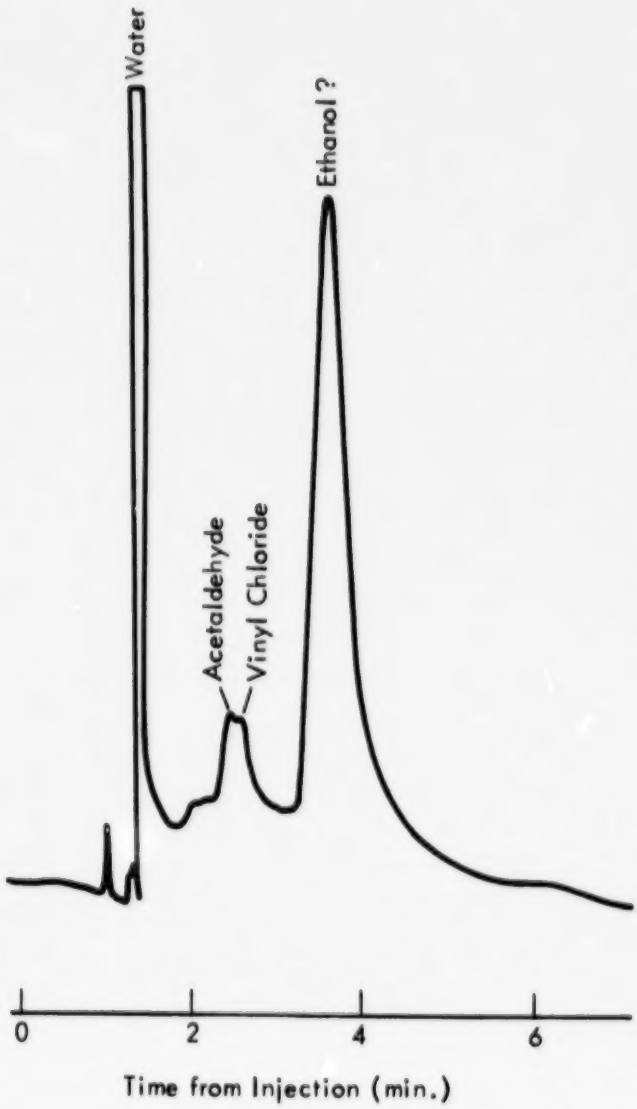

Figure 6. Analysis of condensate sample from June 8, 1976, on platform sample. Chromatogram run on 2 m Chromosorb 102/ 2 m SF-96 column at 110°C

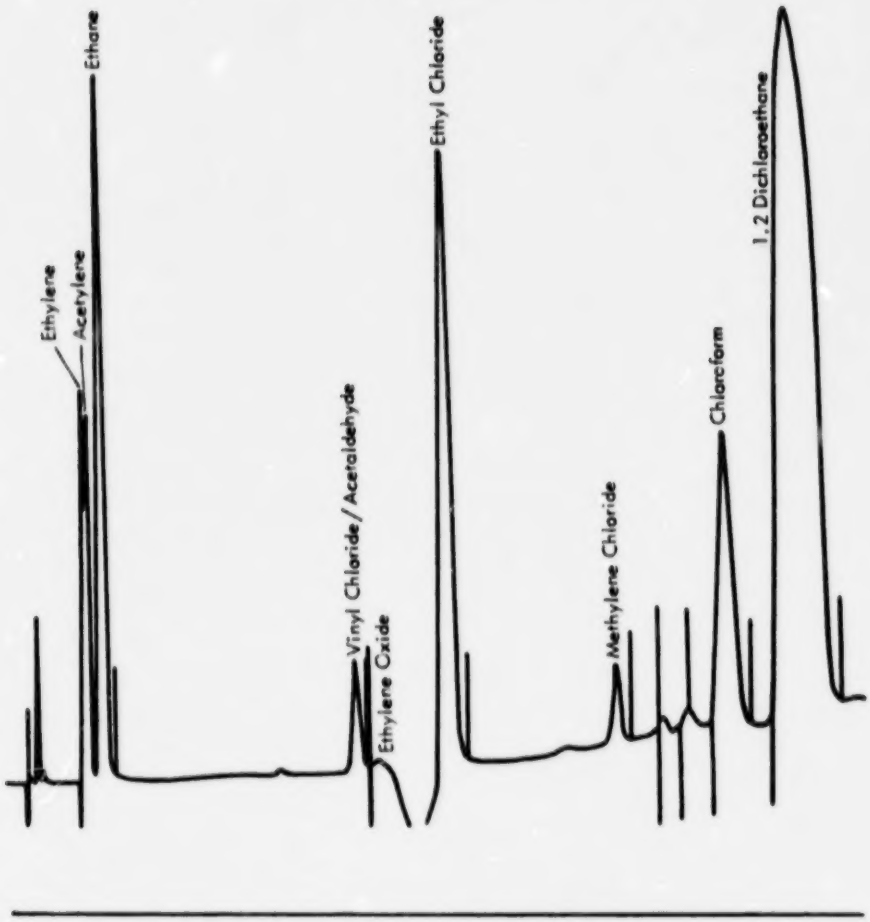

Figure 7. Temperature programmed chromatogram showing major components of the oxychlorination vent. Courtesy of Shell Chemical

APPENDIX A

METHOD 106 - DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES
FEDERAL REGISTER PROCEDURE (PROPOSED)

METHOD 106—DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability.

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethylene) is subjected to chromatographic analysis, using a flame ionization detector.

1.2 The method is applicable to the measurement of vinyl chloride in stack gases from both vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

2. Range and Sensitivity.

The lower limit of detection will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg.

3. Interferences.

In the course of a study to identify the interference potential of several hydrocarbons associated with vinyl chloride, none were found to prevent resolution of the vinyl chloride peak with the Chromosorb 102[1] column. However, if resolution of the vinyl chloride peak is not satisfactory for a particular sample, then chromatograph parameters may be altered with prior approval of the Administrator. If there is reason to believe that some other hydrocarbon with an identical retention time is present in the sample, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, should be performed.

4. Apparatus.

4.1 Sampling (Figure 1).

4.1.1 Probe—Stainless steel, Pyrex glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line—Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 1.

4.1.4 Tedla bags, 100 liter capacity—To contain sample.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle valve—To adjust sample flow rate.

4.1.7 Pump—Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube—To prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flow meter—For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 Connecting tubing—Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 1).

4.1.11 Pitot tube—Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.2 Sample recovery.

4.2.1 Tubing—Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas chromatograph—With flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 Chromatographic column—Stainless steel, 2.5 m × 3.2 mm, containing 80/100 mesh Chromosorb 102.

4.3.3 Flow meters (2)—Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators—For required gas cylinders.

4.3.5 Thermometer—Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer—Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump—Leak-free. Minimum capacity 100 ml/min.

4.4 Calibration.

4.4.1 Tubing—Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags—Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe—0.5 ml, gas tight.

4.4.4 Syringe—50-µl, gas tight.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to ±1%, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch—Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas—Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas—Zero grade.

5.1.3 Oxygen gas—Zero grade.

5.2 Calibration.

5.2.1 Vinyl chloride, 99.9+%—For preparation of standard gas mixtures.

5.2.2 Calibration cylinders (3), optional—One each of 50, 10 and 6 ppm vinyl chloride in nitrogen with certified analysis.

5.2.3 Nitrogen gas—Zero grade, for preparation of standard gas mixtures.

6. Procedure.

6.1 Sampling. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

[1] Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

6.2 Sample storage. Sample bags must be kept out of direct sunlight. When at all possible, analysis is to be performed within 24 hours of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0-100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 155° C, the detector temperature to 225° C, and the sample loop temperature to 70° C. When optimum hydrogen and oxygen flow rates have been determine, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 15 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, A_m, by use of the automatic integrator. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.

7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 µl of 99.9 + % vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. This gives a concentration of 50 ppm of vinyl chloride. In a like manner use the other syringe to prepare dilutions having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases.

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3, above. Set attenuator to X 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time. Record.

7.3 Preparation of chromatograph calibration curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 7.1) using conditions identical with those listed in Section 6.3 above. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record C_s, the concentrations of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_s, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5%, then plot these points vs C_s. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.4 Tedlar bag leak checks. Before each use, make sure a bag is leak-free by checking it for leaks. To leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak.

(NOTE: An alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.)

8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_s = A_m A_f$$

Equation 106-1

where:

A_s = The sample peak area.
A_m = The measured peak area.
A_f = The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3, above, select the value of C_s that corresponds to A_s, the sample peak area. Calculate C_b as follows:

$$C_b = \frac{C_s P_r T_s}{P_s T_r}$$

Equation 106-2

where:

C_b = The concentration of vinyl chloride in the bag sample in ppm.
C_s = The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.
P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.
T_s = The sample loop temperature on the absolute scale at the time of analysis, °K.
P_s = The laboratory pressure at time of analysis, mm Hg.
T_r = The reference temperature, the sample loop temperature recorded during calibration, °K.

9. References.

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia, June 24, 1974.

2. "Evaluation of A Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report oN. 75-VCL-1.

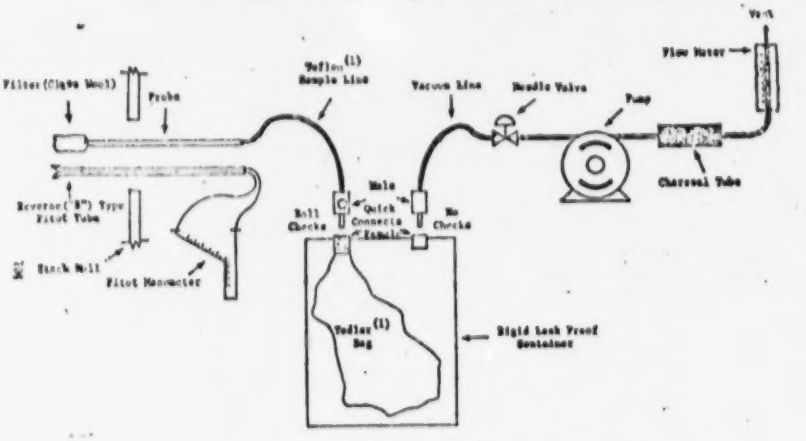

Figure 106-1. Integrated bag sampling train.

(1) Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

APPENDIX B

METHOD 106 - DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES
MRI MODIFIED PROCEDURE

December 3, 1976

METHOD 106 - DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to chromatographic analysis using a flame ionization detector.

1.2 The method is applicable to the measurement of vinyl chloride in stack gases from both vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter. Care must be exercised to prevent undue exposure of sampling personnel to vinyl chloride.

2. Range and Sensitivity

The lower limit of detection will vary according to the chromatograph used. Values reported include 1×10^{-10} g and 4×10^{-10} g.

3. Interferences

Retention indices for several possible interferences are given in Table B-1. The only known serious interferences on the normal chromatographic column are acetaldehyde (vinyl alcohol) and ethylene oxide, which can occur in monomer streams, ambient air, and some copolymer operations. If resolution of the vinyl chloride peak is not satisfactory for a particular sample, then chromatograph parameters may be altered with prior approval of the administrator.

4. Apparatus

4.1 Sampling (Figure 1)

4.1.1 Probe - Stainless steel, Pyrex* glass, or Teflon* tubing according to stack temperature, equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line - Teflon, 6.4 mm diameter, of sufficient length to connect probe to bag.

4.1.3 Male (2) and Female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 1.

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* Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

TABLE 8-1. RETENTION INDICES FOR POSSIBLE VINYL CHLORIDE INTERFERENCES

	2 m Chromosorb 102 100°C	2 m Chromosorb 102 + 1 m Porapak T 120°C	2 m Chromosorb 102 + 2 m SF-96 120°C	2 m Chromosorb 102 + new 2 m SF-96 120°C
Methane*	100	100	100	100
Ethylene	180	180	175	-
Ethane*	200	200	200	200
Propane*	300	300	300	300
Methyl chloride	320	340	320	325
Methanol	330	395	350	375 (low levels retained)
Acetaldehyde	355	400	375	400 (low levels retained)
Ethylene oxide	355	395	375	- (low levels retained)
Vinyl chloride	360	375	360	360
Isobutane	380	380	380	380
Isobutylene	395	395	385	390
1-Butene	395	395	395	-
n-Butane*	400	400	400	400
1,3-Butadiene	400	410	395	395
trans-2-Butene	400	410	400	-
Ethanol	415	475	435	-
Ethyl chloride	415	430	415	410
cis-2-Butene	415	415	410	-
1,1-Dichloroethylene	480†	490†	480†	-
trans-1,2-Dichloroethylene	510†	495†	505†	-

* Reference compounds for indices.

† Column at 150°C.

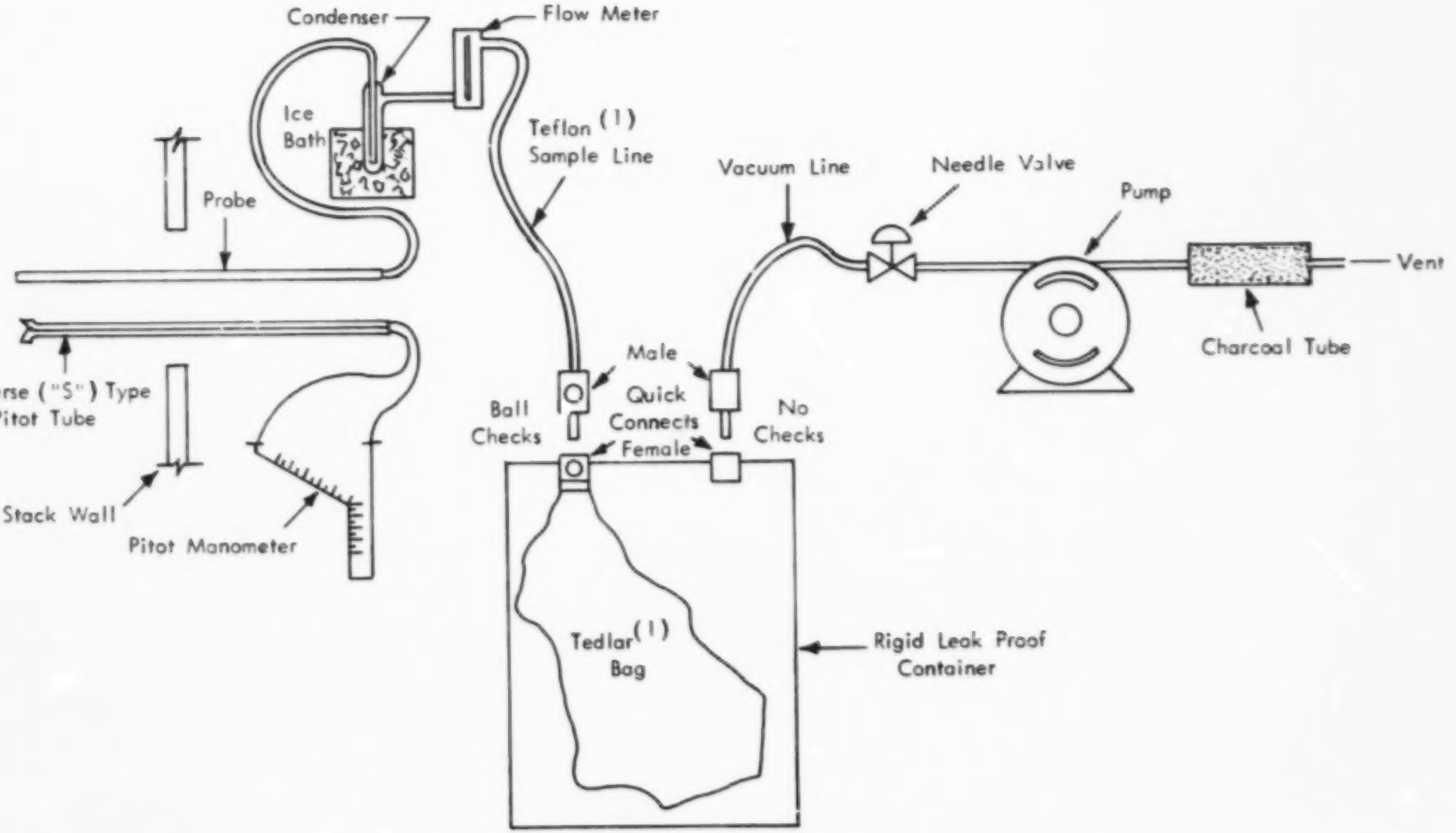

Figure B-1. Integrated bag sampling train

(1) Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

4.1.4 Tedlar* bag, 100 liter capacity. Teflon* bags are not acceptable. Aluminized Mylar* bags may be used provided the samples are analyzed within 24 hours after collection.

4.1.5 Rigid leakproof container for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle valve - To adjust sample flow rate.

4.1.7 Pump - Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube - To prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flowmeter - For observing sample flow rate; capable of measuring a flow range from 100 to 1,000 ml/min. The flowmeter and its fittings must be made of glass or stainless steel.

4.1.10 Connecting tubing - Teflon, 6.4 mm diameter, to assemble sample train (Figure 1).

4.1.11 Pitot tube - Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.1.12 Condenser - Glass vacuum trap, 25 x 200 mm with 10 mm connecting tubes, immersed in an ice bath. Required only if condensation can occur from the sample stream at ambient temperatures. Teflon* fittings should be used to connect the condenser.

4.2 Sample Recovery

4.2.1 Tubing - Teflon, 6.4 mm diameter, to connect bag to gas chromatograph sample loop. Discard the tubing if it shows any contamination (should be checked periodically by sampling a purified nitrogen stream with the tubing and checking the chromatogram). The tubing should be replaced if condensation occurs or if a very high (> 300 mg/m^3) level of vinyl chloride is sampled, to be followed by samples near 3 mg/m^3 (1 ppm).

4.3 Analysis

4.3.1 Gas chromatograph - With flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in sample valve.

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* Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

4.3.2 Chromatographic column - Stainless steel, 2.0 m x 3.2 mm O.D.,* containing 80/100 mesh Chromosorb 102. A secondary column of 20% SF-96 on AW Chromosorb P, 60/80 mesh, stainless steel column, 2 m x 3.2 mm O.D., or Porapak T, 80/100 mesh, stainless steel column, 1.0 m x 3.2 mm O.D., may be required to separate acetaldehyde from vinyl chloride. If used, the secondary column is added after the Chromosorb 102 column. Both secondary columns separate the acetaldehyde/vinyl chloride peaks with the acetaldehyde eluting after vinyl chloride. The combined columns should be operated at 120°C.

4.3.3 Flow meters (2) - Rotometer type, 0 to 100 ml/min capacity.

4.3.4 Gas regulators - For required gas cylinders.

4.3.5 Thermometer - Accurate to one degree centigrade. To measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer - Accurate to 500 Pa (5 mm Hg). To measure atmospheric pressure around gas chromatograph during sample analysis.

4.4 Calibration

4.4.1 Tubing - Teflon, 6.4 mm diameter, for collecting calibration cylinders to sample loop.

4.4.2 Regulator(s) - For vinyl chloride calibration gases.

4.4.3 Needle valve(s) - For flow control from calibration cylinders.

5. Reagents (It is intended that all reagents be of chromatographic grade.)

5.1 Analysis

5.1.1 Helium gas or nitrogen gas - Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas - Zero grade

5.1.3 Breathing air

5.2 Calibration

5.2.1 Calibration cylinders (3). One each of 150, 30 and 15 mg/m^3† (50, 10 and 5 ppm) vinyl chloride in nitrogen with certified analysis. Analysis should be traceable to NBS or to a gravimetrically calibrated vinyl chloride permeation tube.

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* All chromatographic columns used have a wall thickness of approximately 0.5 mm (0.020 in.).

† Specified at conditions of 293°K and 101.3 kPa (760 mm Hg). To convert from parts per million (v/v) to milligrams per cubic meter, multiply by 2.59.

5.2.2 Nitrogen gas - Zero grade

6. Procedure

6.1 Sampling. Assemble the sample train as in Figure 1. Place the probe in the stack and start the pump with the needle valve adjusted to yield a flow of 500 ml/min. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until a rotameter connected to the bag container outlet indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the pump away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag from sunlight.

6.1.1 Tedlar bag leak checks - Before each use, make sure a bag is leak-free by checking it for leaks. To leak check, connect a water manometer and pressurize the bag to 500 to 1,000 Pa (5 to 10 cm water column). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. (Note: An alternative leak check method is to pressurize the bag to 500 to 1,000 Pa (5 to 10 cm water column) and allow to stand overnight. A deflated bag indicates a leak.)

Test the Rigid container for leaks in a similar manner to that for the bag leak check.

Place a rotameter in-line between the Tedlar bag and pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag is empty indicates a leak.

6.2 Sample recovery. With an uncontaminated piece of Teflon tubing connect a bag to the gas chromatograph sample valve. Connect a 0 to 100 ml/min rotameter between the sample valve outlet and the inlet to a small pump with a needle valve flow control.

6.3 Analysis. Set the column temperature to 100°C, the detector temperature to 160°C, and the sample loop temperature to 70°C. When optimum hydrogen and air flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of 40 ml/min has been shown to produce adequate separations. Observe the baseline periodically and determine that the noise level has stabilized and that baseline drift has ceased. Purge the sample loop for at least one minute at

a rate of 50 ml/min, stop the pump, and then activate the sampling valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride. Measure the peak area, A_m, and the peak height, H_m. Record A_m, H_m, and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in height or area more than 5%. The average values will be used to compute the bag concentration.

Compare the ratio of H_m:A_m for the vinyl chloride sample with the ratio for the standard which is closest in concentration. If these ratios differ by more than 10%, the vinyl chloride peak is not pure (acetaldehyde may be present) and the peaks must be resolved (see Section 4.3.2). If the height-area test shows impure peaks, the height measurements will be more accurate than the area measurements. However, the chromatographic conditions should be altered until the height-area test is passed.

7. Calibration

7.1 Determination of vinyl chloride retention time. Perform before and after analyzing bag samples. Establish chromatograph conditions identical with those in 6.3 above. Set attenuator to X 1 position. Flush the sampling loop with zero nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. Flush the sample loop for at least 1 min at the rate of 50 ml/min with the vinyl chloride calibration mixture and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the peak maximum. This quantity, divided by the chart speed, is defined as the retention time. Record.

7.2 Preparation of chromatogram calibration curve. Make a gas chromotographic measurement of each standard gas mixture using conditions identical with those listed in Section 6.3 above. Flush the sampling loop for at least 1 min at the rate of 50 ml/min with each standard gas mixture and activate the sample valve. Record C_c, the concentrations of vinyl chloride injected, the attenuator setting, chart speed, peak area, peak height, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5%, then plot those points versus C_c. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily or before and after each set of bag samples, whichever is more frequent.

8. Calculations

8.1 Determine the sample peak area as follows:

$$A_c = A_m A_f \qquad \text{Eq. 106-1}$$

where:

A_c = The sample peak area

A_m = The measured peak area

A_f = The attenuation factor

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3 above, select the value of C_c that corresponds to A_c, the sample peak area. Calculate C_b as follows:

$$C_b = \frac{C_c P_r T_i}{P_i T_r} \qquad \text{Eq. 106-2}$$

where:

C_b = The concentration of vinyl chloride in the bag sample in mg/m^3.*

C_c = The concentration of vinyl chloride indicated by the gas chromatograph, in mg/m^3.*

P_r = The reference pressure, the laboratory pressure recorded during calibration, kPa (mm Hg).

T_i = The sample loop temperature on the absolute scale at the time of analysis, °K.

P_i = The laboratory pressure at time of analysis, kPa (mm Hg).

T_r = The reference temperature, the sample loop temperature recorded during calibration, °K.

9. Sample Storage

Sample bags must be kept out of direct sunlight. Analysis is to be performed within 24 hours of sample collection.

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* Specified at standard conditions of 293°K and 101.3 kPa (760 mm Hg).

10. References

1. Brown, D. W., Loy, E. W., and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia, June 24, 1974.

2. "Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2. EPA Report No. 75-VCL-1.

Note 1: (Section 4.1.4) The use of Teflon or aluminized Mylar bags has been proposed. Teflon apparently allows excessive permeation through the bag. It has no cost advantage over Tedlar and would not be acceptable. Aluminized Mylar does provide an effective vapor barrier, is much less expensive than Tedlar, nor does it alter vinyl chloride concentrations in the bags up to at least 2 weeks. However, it does tend to outgas various heavy compounds over a period of several days which can contaminate the GC column.

Note 2: (Section 4.1.9) With the rotameter position changed, the pump does not have to be leakfree, nor does the bag container need to be completely leakfree. The change in the rotameter position does require a high quality rotameter but it eliminates most leak problems in the system since it provides a positive check that gas is going into the bag. In this position, the rotameter is also not prone to false high readings from pump pulsations.

Note 3: (Section 5.2) The bag calibration method was deleted because of the safety problems of handling pure vinyl chloride in the field. It is also more difficult to prepare accurate dilutions by this method. Compressed cylinder gases are stable, safer to handle at such concentrations, and more accurate. If special facilities already exist for handling vinyl chloride in the laboratory, either procedure is suitable.

APPENDIX C

METHOD 106 - DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES

Method 106—Determination of Vinyl Chloride from Stationary Sources

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability.

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethylene) is subjected to chromatographic analysis, using a flame ionization detector.

1.2 The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

2. Range and Sensitivity.

The lower limit of detection will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg.

3. Interferences.

Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromosorb 102 column. See sections 4.3.2 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then chromatograph parameters can be further altered with prior approval of the Administrator. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

4. Apparatus.

4.1 Sampling (Figure 1).

4.1.1 Probe—Stainless steel, Pyrex glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line—Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 1.

4.1.4 Tedlar bags, 100 liter capacity—To contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collection.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle valve—To adjust sample flow rate.

4.1.7 Pump—Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube—To prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flow meter—For observing sample flow rate, capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 Connecting tubing—Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 1).

4.1.11 Pitot tube—Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.2 Sample recovery.

4.2.1 Tubing—Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas chromatograph—With flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 Chromatographic column—Stainless steel, 2.0 × 3.2 mm, containing 80/100 mesh Chromosorb 102. A secondary colum of OV SF-96, 20% on 60/80 mesh AW Chromosorb P, stainless steel, 2.0 m × 3.2 mm, will be required if acetaldehyde is present. If used, the SF-96 column is placed after the Chromosorb 102 column. The combined columns should then be operated at 110°C.

4.3.3 Flow meters (2)—Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators—For required gas cylinders.

4.3.5 Thermometer—Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer—Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump—Leak-free. Minimum capacity 100 ml/min.

4.4 Calibration.

4.4.1 Tubing—Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags—Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe—0.5 ml, gas tight.

4.4.4 Syringe—50.0 l, gas tight.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to ±1%, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch—Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas—Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas—Zero grade.

5.1.3 Oxygen gas, or Air, as required by the detector—Zero grade.

5.2 Calibration.

5.2.1 Vinyl chloride, 99.9+%—For preparation of standard gas mixtures.

5.2.2 Calibration cylinders (3), optional—One each of 50, 10 and 5 ppm vinyl chloride in nitrogen, with certified analysis. Analysis must be traceable to NBS (National Bureau of Standards) or to a gravimetrically calibrated vinyl chloride permeation tube.

5.2.3 Nitrogen gas—Zero grade, for preparation of standard gas mixtures.

6. Procedure.

6.1 Sampling. Assemble the sample train as in Figure 106.1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Sample bags must be kept out of direct sunlight. When at all possible, analysis is to be performed within 24 hours of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0-100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 100° C, the detector temperature to 150° C, and the sample loop temperature to 70° C. When optimum hydrogen and oxygen flow rates have been determined verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed

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[1] Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, A_m, by use of H_m and a disc integrator or a planimeter. Measure the peak height, H_m. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5 %. The average value for these two areas will be used to compute the bag concentration.

Compare the ratios of H_m to A_m for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10 %, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2).

6.6 Measure the ambient temperature and barometric pressure near the bag. (Assume 100 percent relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine the record and water vapor content of the bag.

7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 50 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 μl of 99.9+ % vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. This gives a concentration of 50 ppm of vinyl chloride. In a like manner use the other syringe to prepare dilutions having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases.

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3, above. Set attenuator to X 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time. Record.

7.3 Preparation of chromatograph calibration curve. Make a gas chromatographic measurement of each standard gas mixture described in Section 7.1.1 using conditions identical with those listed in Section 6.3 above. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record C_s, the concentrations of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_s, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5%, then plot those points vs C_s. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

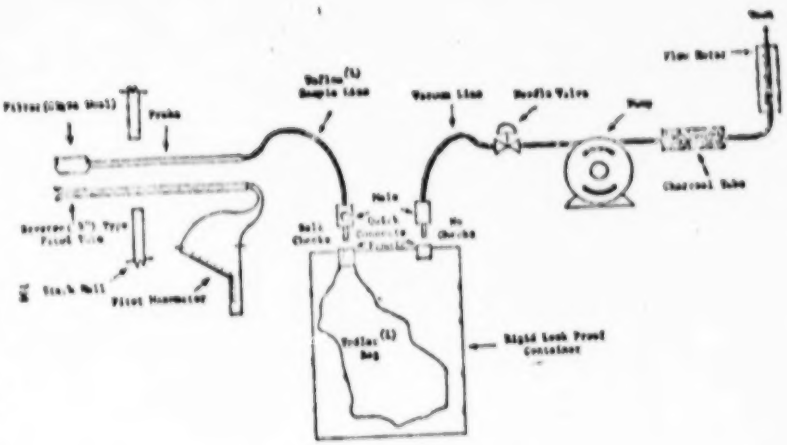

Figure 106-1. Integrated bag sampling train.

(1) Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also check the rigid container for leaks in this manner.

(NOTE: An alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_s = A_m A_f$$

Equation 106-1

where:
A_s = The sample peak area.
A_m = The measured peak area.
A_f = The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3, above, select the value of C_s that corresponds to A_s, the sample peak area. Calculate C_b as follows:

$$C_b = \frac{C_s P_r T_s}{P_s T_r (1 - B_{ws})}$$

Equation 106-2

Where:
B_{ws} = The water vapor content of the bag sample, as analyzed.
C_b = The concentration of vinyl chloride in the bag sample in ppm.
C_s = The concentration of vinyl chloride injected by the gas chromatograph, in ppm.
P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.
T_s = The sample loop temperature on the absolute scale at the time of analysis, °K.
P_s = The laboratory pressure at time of analysis, mm Hg.
T_r = The reference temperature, the sample loop temperature recorded during calibration, °K.

9. References.

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia, June 24, 1974.

2. "Evaluation of A Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974, EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report #EMSL 75-Vc1-1.

3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract No. 68-02-1098, Task Order No. 7.